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A method to determine the Gibbs energy of specific interactions in solutions. Hydrogen bonding of proton donating solutes in basic solvents

Igor A. Sedov, Boris N. Solomonov*

Chemical Institute, Kazan State University, Kremlevskaya 18, Kazan 420008, Russia

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ABSTRACT

One of two fundamental types of solute–solvent intermolecular interactions are the specific interactions, such as hydrogen bonding complexation between solute and solvent. The Gibbs energy of specific interactions is an important quantity that determines rate and equilibrium constants in solutions, but it is difficult to obtain by direct measurement. We proposed equations allowing to determine the contribution of specific interactions to the Gibbs energy of solvation in nonelectrolyte solutions. Applying it for the case of proton donating solutes with one acidic hydrogen atom dissolved in basic solvents, we obtained the values of the Gibbs energies of 1:1 complexation in pure base. These values have been compared with the Gibbs energies of 1:1 complexation in tetrachloromethane. Most of the hydrogen bonds are found to have the same energy in pure base and in CCl_4, however, some weakly bound complexes seem to become even more weakened in pure base medium. Suggested method is applicable in a general situation when multiple associates of different stoichiometry and structure are formed.

1. Introduction

Solute–solvent specific interactions, which are defined as donor–acceptor interactions between Lewis acidic and basic centers of solute and solvent molecules, play an important role in various physico-chemical phenomena. They can be contrasted with the nonspecific interactions—London dispersion forces and polarity/polarizability interactions. Solute–solvent specific interactions strongly influence thermodynamic functions of solution and solvation as well as all other properties of dissolved species. The most common example of specific interactions are hydrogen bonds [1,2]. Hydrogen bonds in solutions are especially significant because of their decisive meaning for chemical processes in live organisms [3].

There were several works aimed to quantify the specific interaction enthalpy between solute and solvent in infinitely diluted solutions of nonelectrolytes from calorimetric data [4–9]. It was found that the specific interaction enthalpies of H-donors in basic solvents are close to the enthalpies of 1:1 hydrogen bonding complexation in tetrachloromethane even for most polar bases [4]. Recently, Solomonov et al. [10] suggested a novel general method to separate the specific interactions contribution from the enthalpy of solution/solvation. It allowed to calculate the enthalpy of specific interactions between solute and solvent for a wide range of systems, including a particularly interesting case of the enthalpy of self-association of aliphatic alcohols. However, there were no methods allowing to calculate the Gibbs energy of solute–solvent specific interactions. There are several models (UNIFAC [11], LSER [12,13], CODESSA [14], COSMO-RS [15], SPACE [16], SMx [17]) that can successfully predict the Gibbs energies of solvation and limiting activity coefficients for large sets of various solutes and solvents, including those with solute–solvent specific interactions. However, these models do not focus on separation of the hydrogen bonding interaction contribution. For example, though LSER and CODESSA models contain acidity/basicity parameters and parameters of other types of interactions (electrostatic, polarization, and dispersion) of a solute, there are also a number of adjustable parameters of solvent, which are optimized in order to fit solvation energy the best. As a result, hydrogen bonding energy can be partially redistributed between other terms in equations. The hydrogen bonding terms present in such models are not considered separately from other terms neither compared with experimental Gibbs energies of hydrogen bonding.

Experimental studies of complexation equilibria between noncharged molecules are usually carried in inert solvents by spectroscopic means. The techniques for determining association constants developed along with the development of spectroscopic methods [18,19]. IR-spectroscopy is the oldest and the most widely used experimental method. One should measure the intensities of bound and unbound bands at different concentrations of one or both of the complexing agents. In some cases, if measurements are carried for a series of structurally close compounds with the

* Corresponding author. Tel.: +7 8432315346; fax: +7 8432315346.
E-mail addresses: igor_sedov@inbox.ru (I.A. Sedov), Boris.Solomonov@ksu.ru (B.N. Solomonov).

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